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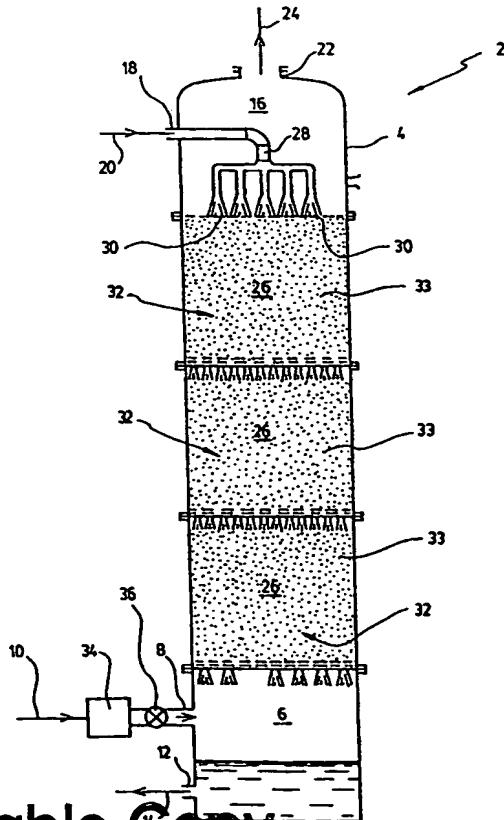
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(75) Inventors/Applicants (for US only): BLAIS, Réjean [CA/CA]; 5915, Saint-Laurent, Lévis, Québec G6V 3V6 (CA). ROGERS, Peter, A. [CA/CA]; 1091, boulevard Pie XI Sud, Val-Bélair, Québec G3X 1J9 (CA).		With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.
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(54) Title: PROCESS AND APPARATUS FOR THE TREATMENT OF CARBON DIOXIDE WITH CARBONIC ANHYDRASE

(57) Abstract

A process is disclosed for the extraction, production and purification of carbon dioxide gas. The process may also be employed for the production of aqueous and/or organic solutions of bicarbonate ions using a precursor feed stream of gas containing carbon dioxide. The process consists of the countercurrent flushing of a packed tower-type bioreactor with gas containing carbon dioxide and a liquid solvent. The bioreactor contains carbonic anhydrase covalently bound to an inert inorganic support. The carbon dioxide of the gaseous phase diffuses into the liquid phase. The immobilized carbonic anhydrase catalyses the hydration of the carbon dioxide which forms hydrogen and bicarbonate ions. The solution of ions may be employed directly or, alternatively, subjected to an ion-exchange resin to immobilize the bicarbonate ions. The aqueous solution of hydrogen and bicarbonate ions may also be recirculated into a second identical bioreactor, wherein they are catalytically converted to water and carbon dioxide.



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PROCESS AND APPARATUS FOR THE TREATMENT OF CARBON DIOXIDE WITH CARBONIC ANHYDRASE

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FIELD OF THE INVENTION

The present invention relates generally to a process for the extraction, production and purification of carbon dioxide gas. More particularly, it relates to the use of a biological molecule, namely carbonic anhydrase, to effect the reversible hydration of carbon dioxide. Carbonic anhydrase can be used for the production, 10 purification of carbon dioxide and the products of the hydration reaction, hydrogen and bicarbonate ions. Specifically, the invention relates to a process whereby immobilized carbonic anhydrase contained within a reactor device catalyses the reversible hydration of carbon dioxide. The invention also relates to an apparatus for performing the process. The process may be employed for the production of 15 hydrogen and bicarbonate ions.

BACKGROUND OF THE INVENTION

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Carbonic anhydrase (EC 4.2.1.1.) is a globular zinc metalloenzyme of molecular mass 30,000. The enzyme was discovered in 1933 and has been the subject of intense scientific investigation. Multiple isoforms have been discovered in plant and animal tissues. The enzyme also exists in plant tissues where it is believed to facilitate the transport of carbon dioxide. Red blood cells contain isoenzymes I and 25 II, which are the most active. Carbonic anhydrase II has the highest molecular turnover number of any known enzyme. One molecule of carbonic anhydrase can hydrate 36,000,000 molecules of carbon dioxide in a period of 60 seconds. Physiologically, carbonic anhydrase facilitates the removal of carbon dioxide from the mammalian body. The general enzyme reaction is shown below in equation 1.

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Equation 1:



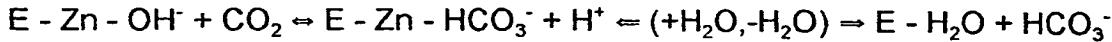
5 It is now generally accepted that the reaction occurs as two half reactions shown below in equations 2 and 3.

Equation 2:



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Equation 3:



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Carbonic anhydrase has been used in many studies directed at improving or testing of various methods of protein immobilization. The high molecular turnover rate of the enzyme renders it an ideal protein for these types of experiments.

20

The presence of carbonic anhydrase in solution facilitates the transfer of carbon dioxide from the gas to the liquid phase. This effect is based on the well established laws governing the mass transfer of gases.

25

The management of carbon dioxide has begun to attract the attention of the scientific community, due primarily to the problem of global warming. Previous interest in carbon dioxide has been centered around the use of the gas in a variety of industrial processes. None of the currently employed carbon dioxide management systems involve enzymatic conversion of the gas and are therefore not relevant to the present application. Prior art processes for the management of carbon dioxide are described in the following US documents: 3,659,400; 3,853,712; 4,032,616; 4,047,894; 4,162,298; 4,452,676; 4,521,387; 4,710,362; 5,061,455; 5,112,740; 5,609,838; 5,618,506; 5,624,812; 5,665,319; 5,674,463; and 5,690,099.

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Moreover, the United States Air Force carried out two investigations in 1965 and 1966 on the possible use of carbonic anhydrase to remove carbon dioxide from

space vehicles. The first study explored the absorption of carbon dioxide from an air stream using a closed air loop apparatus. A variety of chemicals alone and/or in combination with CA were evaluated, with respect to their capacity to remove carbon dioxide. The principal conclusion drawn was that the closed air loop system provided an adequate method to study the removal of carbon dioxide from a stream of air. The second study was directed at determining the efficiency of carbon dioxide removal from an air stream using carbonic anhydrase in the presence of various amines. The conclusion reached was that enzymatic amine solutions could possibly be used for carbon dioxide absorption and desorption in atmosphere control concepts.

Although many studies relating to the management of carbon dioxide have been conducted in prior art, there is still presently a need for a process and an apparatus that will efficaciously manage carbon dioxide rapidly and at a relatively low cost either for producing carbon dioxide or removing it from a CO₂-containing gas.

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SUMMARY OF THE INVENTION

An object of the present invention is to propose a process and an apparatus that will satisfy these needs.

In accordance with the present invention, that object is achieved with a process for removing CO₂ from a CO₂-containing gas, characterized in that it comprises the step of:

a) contacting the CO₂-containing gas with an aqueous liquid, preferably water, in a bioreactor containing immobilized carbonic anhydrase, or an analog thereof, the carbonic anhydrase catalysing the hydration of the CO₂ into hydrogen ions and bicarbonate ions.

Preferably, prior to step a), there is a step of immobilizing carbonic anhydrase in the bioreactor. The step of immobilizing carbonic anhydrase in the bioreactor may comprise the step of covalently binding carbonic anhydrase to an inert solid support material mounted in the bioreactor. The step a) of contacting the CO₂-containing gas with an aqueous liquid comprises the steps of directing a stream of the CO₂-containing gas upwards into the bioreactor and directing a stream of the aqueous

liquid downwards such that the stream of CO₂-containing gas flows countercurrent to the stream of the aqueous solution.

According to a first preferred embodiment of the present invention, the process comprises, after step a), step b) of feeding the hydrogen ions and bicarbonate ions obtained in step a) into a second bioreactor containing immobilized carbonic anhydrase which catalyses the conversion of the hydrogen ions and the bicarbonate ions into concentrated CO₂ and water.

According to a second preferred embodiment of the invention, the process comprises, after step a), the step of feeding the hydrogen ions and bicarbonate ions obtained in step a) into an ion exchanger containing hydroxyl ions so that the carbonate ions are exchanged for the hydroxyl ions which are then free to combine with hydrogen ions to form water.

The present invention also relates to an apparatus for the management of CO₂ using immobilized carbonic anhydrase or analog thereof. The apparatus comprises an upright bioreactor for growing carbonic anhydrase therein.

The bioreactor comprises a bottom chamber having a gas inlet to receive a CO₂-containing gas and a liquid outlet to evacuate from the bioreactor a liquid solution containing hydrogen ions and bicarbonate ions produced in the bioreactor. The bioreactor further comprises an upper chamber having a liquid inlet to receive an aqueous liquid and a gas outlet to evacuate any gas from the bioreactor.

A reaction chamber is disposed between and is in fluid communication with the bottom chamber and the upper chamber. This reaction chamber is characterized in that it comprises a plurality of inert organic supports mounted therein for covalently immobilizing carbonic anhydrase.

In use, the CO₂-containing gas is fed through the gas inlet and an aqueous liquid, preferably water, is fed through the liquid inlet. The CO₂-containing gas and the aqueous liquid flows through the reaction chamber where carbonic anhydrase therein catalyses the hydration of CO₂, thereby forming hydrogen ions and carbonate ions. Then, the solution containing the hydrogen ions and bicarbonate ions flows out from the bioreactor via the liquid outlet and the gas free from CO₂ flows out via the gas outlet.

According to a first preferred embodiment of the present invention, the apparatus comprises a second bioreactor in series with the upright bioreactor which is hereinafter called a first bioreactor. The second bioreactor is substantially similar to the first bioreactor. It comprises a liquid inlet connected with the liquid outlet of the first bioreactor for receiving the liquid solution from the first bioreactor.

A reaction chamber is provided for growing carbonic anhydrase. This reaction chamber is in fluid communication with the liquid inlet and comprises a plurality of inert organic supports mounted therein for covalently immobilizing carbonic anhydrase. The reaction chamber is in fluid communication with a gas outlet to evacuate a gas containing carbon dioxide obtained in the chamber.

A liquid outlet is in fluid communication with the reaction chamber to evacuate water obtained in the reaction chamber.

The second bioreactor preferably comprises means for controlling a pressure in the reaction chamber of the second bioreactor.

According to a second preferred embodiment of the present invention, the apparatus further comprises an ion exchanger having an inlet for receiving the liquid solution from the bioreactor.

The present invention is also directed to the use of carbonic anhydrase or analog thereof covalently immobilized in a bioreactor to remove carbon dioxide from a CO₂-containing gas, or to produce hydrogen and carbonate ions, or to the use of carbonic anhydrase or analog thereof covalently immobilized in a bioreactor to produce CO₂ from enriched solutions of hydrogen and bicarbonate ions.

A non restrictive description of preferred embodiments will now be given with reference to the appended drawings.

25

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross-sectional elevational view of a tower-type bioreactor according to a preferred embodiment of the present invention;

Figure 2 is a schematic flow chart of a first preferred embodiment of the process according to the present invention; and

Figure 3 is a schematic flow chart of a second preferred embodiment of the process according to the present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

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During the course of investigating possible uses of carbonic anhydrase for managing carbon dioxide accumulation in submarines, it was noted that covalent immobilization of monomeric enzymes could result in a functional enzyme system of increased stability. Moreover, there has been a dramatic increase in the use of 10 immobilized enzymes in a wide variety of biotechnological applications. Thus, it was reasoned that a bioreactor employing covalently immobilized carbonic anhydrase would provide an efficient biologically based system to manage carbon dioxide.

Referring to Figure 1, an apparatus (2) for the management of CO₂ according to a first preferred embodiment of the present invention is illustrated. This apparatus (2) is devised primarily to extract or remove carbon dioxide from a CO₂-containing gas and specifically transform this gas to hydrogen and bicarbonate ions. The 15 apparatus (2) comprises an upright bioreactor (4) for growing carbonic anhydrase therein. The bioreactor (4) comprises a lower chamber (6) having a gas inlet (8) to receive a CO₂-containing gas (10) and a liquid outlet (12) to evacuate from the bioreactor (4) a liquid solution (14) containing hydrogen ions and bicarbonate ions produced in the bioreactor (4). The bioreactor (4) further comprises an upper 20 chamber (16) having a liquid inlet (18) to receive an aqueous liquid (20) and a gas outlet (22) to evacuate any gas (24) from the bioreactor (4).

A reaction chamber (26) is disposed between the lower chamber (6) and the 25 upper chamber(16). As can be appreciated, the reaction chamber (26) of the bioreactor (4) illustrated is preferably divided in three sub-chambers. The reaction chamber (26) is in fluid communication with the lower chamber (6) and the upper chamber (16). Preferably, the liquid inlet (18) of the upper chamber (16) is connected to a pipe system (28) enclosed therein and having at least one liquid outlet (30) into the reaction chamber (26) such that the aqueous liquid (20) entering the bioreactor 30 (4) flows directly into the reaction chamber (26). The reaction chamber (26) has a

lower surface permeable to gas and liquid such that the stream of CO₂-containing gas entering the bioreactor (4) from the lower chamber (6) flows upwards into the reaction chamber (26) and the liquid in the reaction chamber (26) flows downwards towards and into the lower chamber (6).

5 The reaction chamber (26) is characterized in that it comprises a plurality of inert organic supports, schematically represented in Figure 1 as numeral reference (32), mounted therein for covalently immobilizing carbonic anhydrase (33). These supports (32) are preferably made of ceramic such as silica, namely silica burl saddles or they may be made of polymer such as nylon, polystyrene and polyethylene. The immobilization technique preferably uses one of the following bonding agents: imidocarbonate (silicon), carbodiimide (silica and nylon) and imine (silica and nylon). The polystyrene, nylon and polyethylene may be chemically modified with nitric acid to increase covalent bounding with the amine groups of the enzyme.

15 The CO₂-containing feed gas (10) may consist of ambient air or any gaseous mixture containing carbon dioxide. The gas (10) may be filtered through a conventional filtering means (34) known in the art to concentrate the carbon dioxide and/or remove physical impurities. Control means for controlling the CO₂-containing gas flow (10) through the gas inlet (8) is provided. Thus, the gas (10) is then fed into the lower portion (6) of the bioreactor body (4) using preferably an appropriate valve system (36) for volume and input velocity control. The bioreactor (4) is constructed as a packed tower, a classical design used in numerous applications.

20 The preferably filtered aqueous or organic solvent (20) enters the bioreactor (4) from the upper chamber (16) and flows downwards either by gravity or pressure controlled pumping. In the reaction chamber (26), the carbon dioxide of the input gas (10) will diffuse preferentially into the liquid phase (20) as the carbonic anhydrase transforms the gas into hydrogen and bicarbonate ions. The resulting liquid solution (14) of ions leaves the bioreactor (4) for subsequent use. The unique aspect of the invention is the use of carbonic anhydrase as a means to produce enriched solutions of bicarbonate ions. There are several important variations possible with respect to the configuration of the bioreactor (4). The composition of

the input gas (10) may be varied along with the volume and speed of delivery. The bioreactor (4) may be deployed as a closed system so that the feed gas (10) can be compressed and/or enriched to enhance the kinetics of the mass transfer of the carbon dioxide from the gas to the liquid phase. There is a large number of methods which may be employed to optimize the gas-liquid interaction in the reaction chamber (26), and hence the diffusion of carbon dioxide. The composition (e.g., pH) of the resulting ion solution may be modified according to need. This configuration can serve to extract carbon dioxide from a gas stream to produce a gas or gas mixture free of carbon dioxide.

Referring to Figure 2, this first bioreactor (4) design may preferably be coupled to an anion exchange system (39) with the resin in the hydroxide form. The ion exchanger (39) has an inlet (37) for receiving the liquid solution (14) from the bioreactor (4). Since the carbon dioxide hydration reaction produces hydrogen and bicarbonate ions in equimolar quantities, this solution may be fed directly into the ion exchange system (37). The bicarbonate ions will be exchanged for the hydroxyl ions which will be free to combine with the hydrogen ions to form water. This system could be deployed as a carbon dioxide management system in any closed space such as a submarine. As illustrated in Figure 2, the solution (35) impoverished in hydrogen and bicarbonate ions may be recycled in the bioreactor (4).

Referring to Figure 3, the apparatus (2) for the management of carbon dioxide may further comprise a second bioreactor (38) similar to the first one and connected in series therewith. This particular configuration operates as a closed system. This system serves to produce carbon dioxide and operates in a manner similar to the individual bioreactor design of Figure 1. The liquid solution (14) containing a relatively high concentration of hydrogen and bicarbonate ions produced in the first bioreactor (4) is fed to the second bioreactor (38) in which carbon dioxide is formed in the reaction catalysed by the carbonic anhydrase. This removal of the gas from the aqueous phase may be enhanced by the application of a slight (i.e., 7-9 mm Hg) negative pressure. The concentrated carbon dioxide can then be recovered for subsequent use.

Since this second bioreactor (38) is similar to the first one, it is schematically illustrated as a box in Figure 3. This second bioreactor (38) comprises a liquid inlet (40) connected with the liquid outlet (12) of the first bioreactor (4) for receiving the liquid solution (14) from the first bioreactor (4). The second bioreactor (38) comprises a reaction chamber similar to the reaction chamber (26) of the first bioreactor (4) for growing carbonic anhydrase. The reaction chamber is in fluid communication with the liquid inlet (40) and comprises a plurality of inert organic supports mounted therein for covalently immobilizing carbonic anhydrase. A gas outlet (42) is in fluid communication with the reaction chamber to evacuate carbon dioxide obtained in the chamber. A liquid outlet (44) is in fluid communication with the reaction chamber to evacuate water (46) containing a small amount of hydrogen and bicarbonate ions obtained in the reaction chamber. The second bioreactor (38) may preferably comprise means for controlling a pressure in the reaction chamber.

As can be appreciated, the process and apparatus according to the present invention may be used for the extraction, production and purification of carbon dioxide gas. The process may also be employed for the production of aqueous and/or organic solutions of bicarbonate ions and hydrogen ions using a precursor feed stream of gas containing carbon dioxide. It could be very advantageous to use such process and apparatus in any closed space such as a submarine.

WHAT IS CLAIMED IS:

1. A process for removing CO₂ from a CO₂-containing gas, characterized in that it comprises the step of:

5 a) contacting the CO₂-containing gas with an aqueous liquid (20) in a bioreactor (2) containing immobilized carbonic anhydrase (33) or an analog thereof, the carbonic anhydrase (33) catalysing the hydration of the CO₂, thereby producing hydrogen ions and bicarbonate ions.

10 2. The process according to claim 1, characterized in that it further comprises, prior to step a), a step of:

 growing and covalently immobilizing carbonic anhydrase (33) or an analog thereof in the bioreactor (2).

15 3. The process according to claim 2, characterized in that the step of immobilizing carbonic anhydrase (33) in the bioreactor (2) comprises the step of covalently binding carbonic anhydrase (33) to an inert solid support (32) mounted in the bioreactor (2).

20 4. The process according to anyone of claims 1 to 3, characterized in that it further comprises, after step a), the step of:

 b) feeding the hydrogen ions and bicarbonate ions obtained in step a) into a second bioreactor (38) containing immobilized carbonic anhydrase which catalyses the conversion of the hydrogen ions and the bicarbonate ions into CO₂ and water.

25 5. The process according to anyone of claims 1 to 3, characterized in that it further comprises, after step a), the step of:

 - feeding the hydrogen ions and bicarbonate ions obtained in step a) into an ion exchanger (39) containing hydroxyl ions so that the bicarbonate ions are exchanged for the hydroxyl ions which are then free to combine with hydrogen ions to form water.

6. The process according to anyone of claims 1 to 5, characterized in that step a) comprises the steps of:

5 directing a stream of the CO₂-containing gas upwards into the bioreactor (2) and directing a stream of the aqueous liquid (20) downwards such that the stream of CO₂-containing gas is countercurrent to the stream of the aqueous solution.

7. The process according to anyone of claims 1 to 6, characterized in that it comprises, prior to step a), a step of:

10 filtering the CO₂-containing gas.

8. The process according to anyone of claims 1 to 7, characterized in that the aqueous liquid consists of water.

9. An apparatus for the management of CO₂ comprising:

15 an upright bioreactor (2) containing carbonic anhydrase therein or an analog thereof, the bioreactor (2) comprising:

20 a bottom chamber (6) having a gas inlet (8) to receive a CO₂-containing gas (10) and a liquid outlet (12) to evacuate from the bioreactor (2) a liquid solution (14) containing hydrogen ions and bicarbonate ions produced in the bioreactor (2);

25 an upper chamber (16) having a liquid inlet (18) to receive an aqueous liquid (20) and a gas outlet (22) to evacuate any gas (24) from the bioreactor (2);

30 a reaction chamber (26) disposed between and being in fluid communication with the bottom chamber (6) and the upper chamber (16), the reaction chamber (26) being characterized in that it comprises a plurality of inert solid supports (32) mounted therein for covalently immobilizing carbonic anhydrase (33).

10. An apparatus as claimed in claim 9, characterized in that it further comprises an ion exchanger (39) having an inlet (37) for receiving said liquid solution (14) from the bioreactor (2).

11. An apparatus as claimed in claims 9 or 10, characterized in that it further comprises filtering means (34) for filtering the CO₂-containing gas (10) prior to feeding it to the gas inlet (8).
- 5 12. An apparatus as claimed in anyone of claims 9 to 11, characterized in that it comprises control means for controlling the CO₂-containing gas (10) flow through the gas inlet (8).
- 10 13. An apparatus as claimed in claim 12, characterized in that the control means comprises a valve (36) mounted on the gas inlet.
14. An apparatus as claimed in anyone of claims 9 to 13, characterized in that it comprises a second bioreactor (38) in series with said upright bioreactor (2) which is hereinafter called a first bioreactor (2), said second bioreactor (38) comprising:
 - 15 a liquid inlet (40) connected with the liquid outlet (12) of the first bioreactor (2) for receiving said liquid solution (14) from the first bioreactor (2);
 a reaction chamber containing carbonic anhydrase, the reaction chamber being in fluid communication with the liquid inlet (40) and comprising a plurality of inert support mounted therein for covalently immobilizing carbonic anhydrase;
 - 20 a gas outlet (42) in fluid communication with the reaction chamber (38) to evacuate a gas phase containing carbon dioxide obtained in the chamber (38); and
 a liquid outlet (44) in fluid communication with the reaction chamber (38) to evacuate a liquid phase (46) obtained in the reaction chamber (38).
- 25 15. An apparatus according to claim 14, characterized in that the second bioreactor (38) comprises means for controlling a pressure in the reaction chamber of the second bioreactor.
- 30 16. Use of carbonic anhydrase or an analog thereof covalently immobilized in a bioreactor to remove carbon dioxide from a CO₂-containing gas.

17. Use of carbonic anhydrase or an analog thereof covalently immobilized in a bioreactor to produce CO₂ from enriched solutions of hydrogen and bicarbonate ions.

18. Use of carbonic anhydrase or an analog thereof covalently immobilized in a
5 bioreactor to produce enriched solutions of hydrogen and bicarbonate ions from a CO₂-containing gas.

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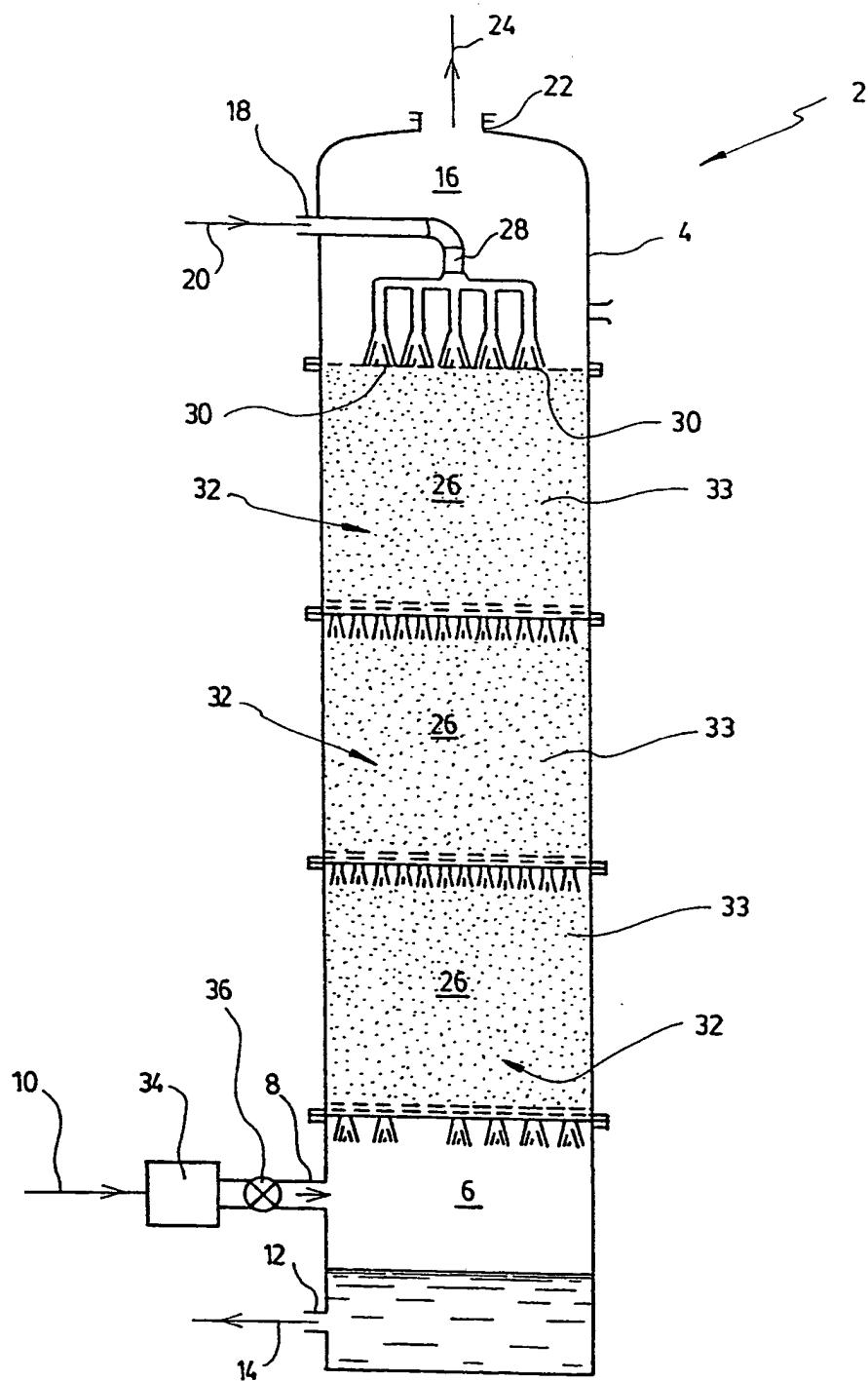
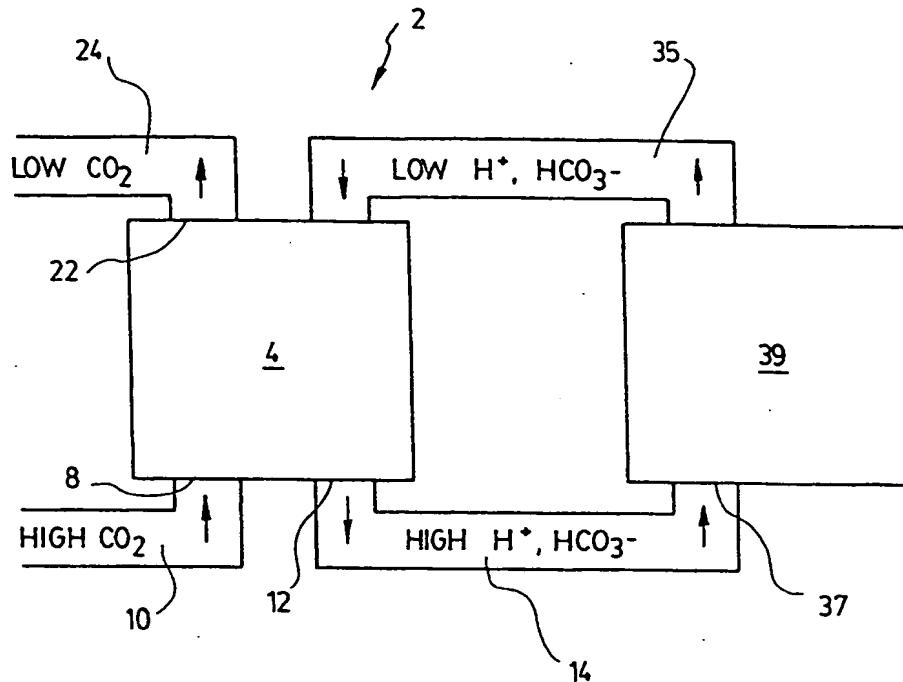
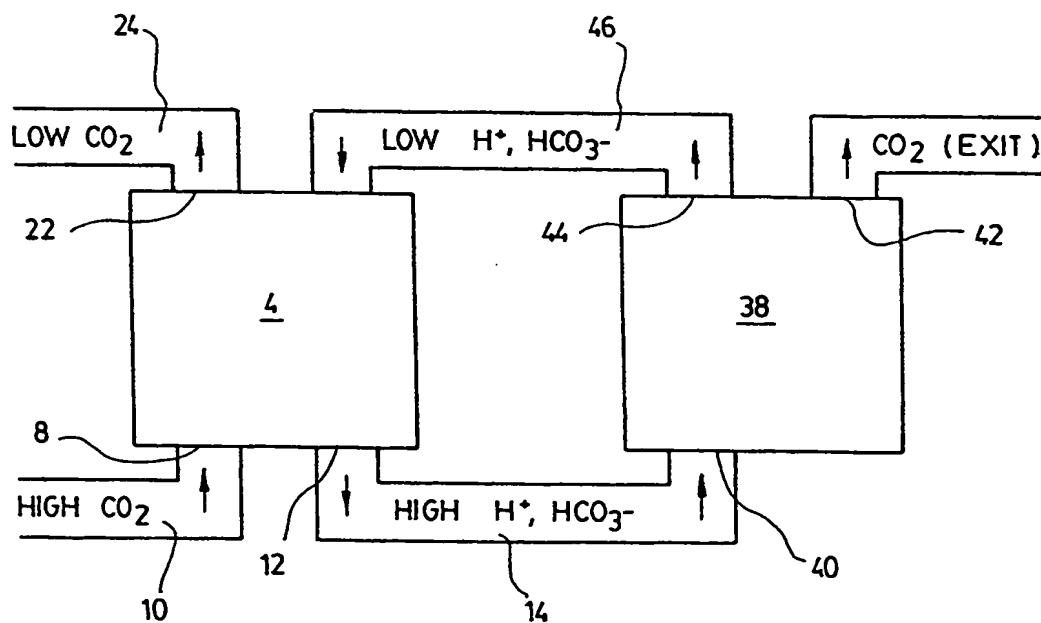


FIG. 1

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FIG. 2FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 96/00541

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 B01D53/62 B01D53/84 C12M1/40

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 B01D C12M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WO 96 40414 A (TRACHTENBERG MICHAEL C) 19 December 1996 see page 4, line 14 - page 5, line 22 see page 9, line 18-30 see example 2</p> <p>---</p> <p>EP 0 511 719 A (AQUANAUTICS CORP) 4 November 1992 see page 25, line 33 - page 26, line 18; figures 5-7 see page 22, line 19-32 see page 23, line 19-47</p> <p>---</p> <p>-/-</p>	1-4, 8, 16-18
X		1-3, 8, 9, 16

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

24 September 1998

Date of mailing of the international search report

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Name and mailing address of the ISA

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Polesak, H

INTERNATIONAL SEARCH REPORT

Inte [redacted] Application No

PCT/CA 98/00541

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 9724 Derwent Publications Ltd., London, GB; Class D15, AN 97-260037 XP002078598 & CN 1 101 626 A (HU Y) see abstract</p> <p>-----</p>	18

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l application No

PCT/CA 98/00541

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